

**REMARKS**

Reconsideration is respectfully considered in light of the remarks which follow.

Claims 1, 3-7 and 10-11 are before the Examiner.

No claims have been amended.

Claims 1-7 and 9-11 are rejected under 35 U.S.C. 103(a) as being unpatentable over CA 2,223,377 taken in view of Vanell (6,423,638) or Hall et al. Applicants respectfully traverse.

The process claims and the product claims are separately addressed below.

**Process Claims 4-7 and 10**

**Claim 10**

Claim 10 employs "consisting of" and is closed to the presence of additional material steps, e.g. filtration. The recovered product, in short, is achieved without the need of a filtration step.

CA 2,223,377 does not teach a two step process where a product like that claimed is recovered. CA 2,223,377 does not teach the claimed process conditions. The reaction conditions taught in Example 5 of CA 2,223,377 differ from those exemplified in the instant specification, e.g. additional oxygen and specific amounts of reagents are employed.

CA 2,223,377 does not teach a relationship between particle size distribution and potassium salt concentration or the potassium concentration. There is no mention in CA 2,223,377 of the morphology of the doped pyrogenic particles or changes therein. Further, CA 2,223,377 does not teach a relationship between particle morphology and potassium salt concentration or the potassium concentration. In short, there is no teaching of potassium salt

concentration or the potassium concentration as result dependent variable in terms of a property, e.g. particle morphology, particle size distribution. It is not seen why one would select and optimize potassium salt concentration or the potassium concentration to better a property without the disclosure of a correlation between concentration and an affect on that property.

Claim 10 requires the recovery of a specified product comprising pyrogenic-doped oxide particles having a breadth of particle distribution of at least 0.7 after its formation without the need of a filtration or any other significant intervening step. Common sense suggests one must know of the existence of the named product to recover it. There is no teaching of the claimed product by CA 2,223,337. Further, the experimental conditions employed in Example 5 of CA 2,223,337 are different from those of the instant specification where there is added oxygen present in Example 5 of CA 2,223,337. It would seem to be quite speculative to assume that the CA 2,223,337 Example 5 product is inherently the same as that claimed since the experimental conditions are different. (The anticipatory grounds of rejection were previously withdrawn.)

Withdrawal of the rejection is respectfully requested in light of the closed language "consisting of" and the arguments above .

#### Claim 4-7

Claim 4 employs "comprising" and is therefore open to the presence of additional steps. Claim 4 requires the presence of a potassium salt concentration more than 0. 5% by wt. and requires the recovery of a potassium doped pyrogenically produced silica particles having the

claimed narrow range of particle sizes and also having the specified concentration of potassium distributed equally within the particles.<sup>1</sup>

Example 5 of CA 2,223,337 employs a solution of 0.5% aqueous solution of potassium chloride.<sup>2</sup> There are numerous other process conditions possible. While example 5 is directed to doping of pyrogenic silica with potassium, there is no further characterization of the except for the description appearing in Table 2 and that appearing in the example itself, e.g. BET surface area of 199 m<sup>2</sup>/g. There is no mention of particle size distribution nor particle morphology.

The Examiner indicates that both Hall et al<sup>3</sup> and Vanell<sup>4</sup> are employed to show the desirability of narrow particle distribution ranges in polishing applications. Neither reference teaches a correlation between particle size distribution and potassium salt concentration or the potassium concentration or a correlation between particle morphology and potassium salt

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<sup>1</sup> The instant specification discusses the unexpected nature of the morphological changes in potassium doped pyrogenically produced silica particle first seen at a minimum potassium concentration. The morphological change in particle concentration permits one to achieve the claimed narrow particle size distribution in a two step process without the need of filtration. Such a narrow distribution of particle sizes was not recognized for potassium doped pyrogenically produced silica prior to Applicants.

<sup>2</sup> Please note that the claims exclude this amount and that the instant examples specify higher concentrations.

<sup>3</sup> Hall et al is concerned with functionalized oxides (chemically treated oxides) in the context of abrasives to be used in CMP. The functionalization imparts stability to the particles in alkaline environments by preventing degradation.

<sup>4</sup> Vanell is concerned with the development of a filter capable of use with a colloidal suspension in real-time. Vanell achieves this, in part, by breaking apart agglomerates prior to filtering. See col. 4, lines 43-52. The materials mentioned by Vanell as applicable for their approach are silicon dioxide particles formed either by chemical vapor deposition of SiCl<sub>4</sub> or by colloidal methods. These particles form aggregates having sizes of at least 150 nanometers. See col. 15, lines 45-59. Vanell clearly states that 1) the well known processes of filtering are inadequate for filtering colloidal suspensions because of high particle counts in suspension, 2) filters rapidly blind and plug up and 3) removing too many of the particles can also change the chemistry of the colloidal suspension making it unstable for the application. See col. 19, lines 38-44.

concentration or the potassium concentration. Neither reference mentions doped pyrogenic silica.

The case law cited by the Examiner has been considered. Neither case suggests that one can optimize in a vacuum. The cases suggest that one must know that there is a correlation between a variable and a property one wishes to optimize. Here, there is no stated reason to select potassium salt concentration or the potassium concentration for optimization amongst other possibilities. Further, it is not clear for what property one would optimize potassium salt concentration or the potassium concentration for. Common sense would suggest that without a goal, optimization would not be attempted.

The Examiner next asserts that it would have been obvious to employ the Vanell filtration method to optimize the particle distribution range of CA 2,223,337 product, e.g. narrow the particle size distribution.

This raises some questions: Do the references suggest their combinability? Are the references in fact be capable of being combined without some direction of how to do so? Lastly, Is there an advantage to a "commercial" process which employs one less step and achieves the desired end? (This assumes that the Vanell method is applicable to doped pyrogenic silica. This still remains an issue. )

The combined teachings of the reference on their face do not answer either of the first two questions. The answer to the third is an "unequivocal yes". Why include the expense of an additional step which is not necessary, especially when it is not certain it can operate on the intended mixture.

### Suggestive of the Reference Combination

References are commonly deemed properly combinable when there is a problem apparent in one for which the other teaches a solution. Here there does not appear to be one. There is no mention of a particle size range, broad or narrow, in CA 2,223,337. CA 2,223,337 merely discloses as one use amongst many, the use as a polishing material. See page 4. This application is not described in any detail. Here, it is not clear if the particle size range inherently formed in Example 5 requires or needs attention to be used as a polishing material. The secondary reference does not suggest that there is a problem associated with doped pyrogenic silicas like that of CA 2,223,337 relative to particle size distribution.

Accordingly, it appears that the Examiner suggests any particle size range present in the Example 5 product of CA 2,223,337, whether narrow or wide, needs attention and can be further narrowed by filtration. (Note Vanell teaches that there are downsides to filtration. See background section and col. 19 lines 32-49.) Only colloidal products are exemplified by Vanell. No specific detailed guidance exists as to pyrogenic silica. There may be some unpredictability as to actual benefits to be obtained.<sup>5</sup> There is no mention of doped pyrogenic silica in Vanell.

It should be considered unexpected, based on the art assembled by the Examiner, that one can obtain the claimed particle range without the use of a filtration- like step.

### Guidance

As noted above (see footnote 5), a dispersion of pyrogenic silica is expected to gel over time unless properly treated. A highly viscous liquid would not be expected to be amenable to

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<sup>5</sup> Dispersions of pyrogenic silica unless properly prepared will gel and lose fluidity. See Reference Example 1 of U.S. Patent 5,967,964. See Zhenwu Lin, Joseph Zahka and Geanne Vasilopoulos "POU Filtration of Silica-Based CMP Slurries Using Planatgard <sup>TM</sup> Filters", Mykrolis Applications Note MA071 where filter plugging is discussed.

filtration where easy of flow is required. There is no teaching cited by the Examiner as to how address the viscosity issue. Without this teaching, it is not seen how one would address the problem latent with the Vanell method.

It appears as to the method claims that a proper prima facie case of obviousness has not been established. Withdrawal of the rejection of the method claims is respectfully requested.

### Product Claims 1 and 3

Claim 1, a product by process claim, is directed to potassium doped pyrogenically produced metal or metalloid, e.g. silica, particles having 0.03 to 20% by weight potassium uniformly distributed within the particles and with a "narrow" distribution of particle sizes, breadth of the distribution of particle size of at least 0.7 (One represents a monodispersion.). An actual distribution of particles obtained in Example 7 is shown in Table 4 (pages 26-25) and depicted in figures 11-13. A ninety percent numeric distribution of particles are between about 12 and about 30 nm and a ninety percent weight distribution of particles are between about 14 and 44 nm. A pictorial representation of the particle distribution is shown in figures 11 and 13.

It is not seen that CA 2,223,377 fairly teaches, suggests or renders obvious the product claimed. There is no evidence that the CA 2,223,377 product has the claimed particle size distribution or the claimed potassium concentration uniformly distributed throughout the doped pyrogenically produced particles. (Note the differences in the preparatory methods.) Further, there is no evidence that the CA 2,223,377 particles have the structure denoted by the DBP values associated with claim 3 (Figure 4). Please consider that a morphological change occurs with the claimed threshold concentration of potassium. Also, the examples different

experimental conditions than does Example 5 of CA 2,223,377, reagent amounts and added oxygen.

The secondary references do not deal with potassium doped pyrogenically silica. It is not seen how the secondary references would be suggestive of changes of a "compound", which they do not speak to. It is not a question of "enhanced purity". The claimed product represents a departure from what existed in the art. There is a morphological change in the particles as well as a change in particle distribution. As claimed, the product is distinct from a mere monodispersion.

The references are incomplete in their teachings. They do establish a prima-facie case of obviousness, alone or in combination. The potassium concentration correlates with the properties taught. See page 22 of the specification for a fuller explanation. Withdrawal of the rejection is respectfully requested.

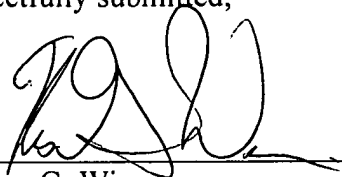
Further, the experimental conditions of the invention, as note above, are distinct from those of Example 5 of CA 2,223,377. The experimental conditions are distinct, therefore the reasonable conclusion to draw is that the product of Example 5 of CA 2,223,377 is distinct from that of the invention.

In view of the foregoing amendments and remarks, the application is believed to be in condition for allowance and a notice to that effect is respectfully requested.

Should the Examiner not find the application to be in allowable condition or believe that a conference would be of value in expediting the prosecution of the application, Applicants request that the Examiner telephone undersigned to discuss the case and afford Applicants an opportunity to submit any Supplemental Amendment that might advance prosecution and place the application in allowable condition.

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Respectfully submitted,

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## Zhenwu Lin, Joseph Zahka and Geanne Vasilopoulos

The typical specification for commercial silica slurries includes percent solids, pH, specific gravity, mean particle size and general (bulk) particle size distribution.

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However, a small number of “large” particles ( $>1\mu\text{m}$ ) have been found which fall outside of the specified size distribution. These particles, which can be aggregates, agglomerates. SEM images shown in Figures 2A and 2B confirm their existence. These large particles may come from agglomeration or local drying of slurry on shipping containers and in the distribution system. Gels may form due to pH shocks during dilution or temperature fluctuations during shipment and storage.

There is no definitive information available on what size or type of particles can cause microscratches and particle contamination on wafer surfaces. However, higher numbers of “large particles” have been found to cause higher incidence of microscratches and particle contamination on polished wafers. Slurry filtration has proven to be beneficial in reducing wafer defects and increasing yields in CMP processes[1].

A control oxide CMP polishing experiment was conducted using a commercial fumed silica slurry contaminated with  $5\text{ }\mu\text{m}$  silica particles ( $\sim 10^4$  particles/ml). The polishing were performed on an IPEC/Westech 472 tool using a standard oxide CMP recipe. The bare wafers were deposited with 1000 nm PECVD  $\text{SiO}_2$  before polishing. Figure 3 and 4 show the surface scan results on the wafers polished with and without point-of-use filtration. A ten-fold reduction of light point defects was achieved by using a Planargard CMP5 filter at the POU.

**Slurry Characterization**

The main challenge of slurry filtration is to selectively retain the small number of defect-causing “large” particles (i.e.,  $10^4$  to  $10^6$  counts/ml greater than  $1\text{ }\mu\text{m}$ ) without retaining the desirable, small particles (30 to 200 nm) present in very high concentration ( $> 10^{15}$  counts/ml). There should be no measurable changes to the slurry’s percent solids concentration and bulk particle size distribution before and after filtration. Therefore, filters to be used in CMP slurry filtration should be evaluated *in slurry* to validate their performance for the following attributes:

- Retention efficiency for “large” particles
- % solids content and bulk particle size distribution before and after filtration
- Throughput (Lifetime)

**1. Detection of “Large” Particles**

Quantitative determination of “large particles” is required to determine filter retention and a correlation between large particle concentration and wafer defects. There is no commercial particle counters available that can be used to detect the large particles ( $10^4$  to  $10^6$  counts/ml  $>1\text{ }\mu\text{m}$ ) in the presence of bulk slurry particles ( $> 10^{15}$  counts/ml), without substantial sample dilution. Various particle counters were evaluated to determine their ability to detect the large particles with maximum tolerance to high concentrations of small particles (minimum sample dilution) and with ease of

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operation. We selected a light scattering instrument was selected for the slurry application.

A typical schematic of the particle counting system, shown in Figure 5, includes continuous on-line dilution of slurry. The dilution factor should be high enough to minimize the interference caused by small particles in the slurry. Figure 6 shows a typical profile of large particle concentrations in oxide slurry before and after filtration. Filter retention for particles of a specific size can then be calculated based on the particle concentration before and after filtration.

**2. Measurement of Bulk Particle Size Distribution and Percent Solids**

Bulk particle size distribution (PSD) can be measured by many techniques [4]. The two most commonly used techniques in CMP slurries are light scattering and chromatography (i.e., capillary hydrodynamic fractionation, (CHDF). The light scattering instrument used for slurry PSD measurement is based on photon correlation spectroscopy (PCS), also referred to as quasi-elastic light scattering (QELS) or time-dependent light-scattering. With PCS, the size information is obtained from the time dependent fluctuation of scattered intensity due to concentration fluctuations resulting from Brownian motion of particles[4].

CHDF is based on the size exclusion effects that occur when a dispersion of particles flows through a capillary tube. Laminar flow in the capillary tube has a parabolic velocity profile. Smaller particles can reach the slower streamline close to the tube wall due to Brownian motion, while larger particles cannot. Therefore, large particles exit the capillary tube faster than smaller ones. CHDF can be used to measure particles between 15 nm and 1 micron with up to 1% solids [5]. This method was used for slurry particle size distribution measurement.

Another PSD instrument is based on acoustic attenuation spectroscopy. When acoustic waves propagate through a medium with suspended particles, the acoustic beam will be further attenuated by the particles by a variety of mechanisms. The acoustic attenuation spectrum can be detected and then inverted to obtain a mean particle size, a particle size distribution, and a dispersion concentration.

The percent solids in slurry can be calculated by drying a slurry sample of known weight.

**Performance of Planargard Filters**

Filter performance should be evaluated in slurry to determine: (a) retention efficiency for large particles; (b) percent solids content and bulk particle size distribution before and after filtration; (c) filtration throughput. This information is necessary for CMP process engineers to implement proper filtration.

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Conventional microporous membrane filters will not work due to the high solids concentration in the slurry that forms a cake and plugs membrane quickly. Graded-density non-woven depth filters are preferred for this application. Filtration experiments were conducted with all-polypropylene graded-density Planargard™ filters using silica slurry in a single-pass configuration to simulate point-of-use applications. Feed and filtrate samples were taken and analyzed for large particle concentration, percent solids, and bulk particle size distribution. The filter retention efficiency is defined as:

$$\text{Retention} = \frac{\text{Concentration in feed} - \text{Concentration in filtrate}}{\text{Concentration in feed}} \times 100\%$$

The retention efficiency curves for various Planargard filters are shown in Figure 7.

Throughput was measured based on the differential pressure across the filter as a function of filtered volume. A typical plugging curve is illustrated in Figure 8, which shows a gradual increase in differential pressure across the filter. The differential pressure increases slowly initially, but then climbs rapidly as the filter reaches the end of life. Data analysis proves that the plugging process follows the complete plugging mechanism, which can be represented by a linear relationship between the inverse differential pressure across the filter (or  $\Delta P_{\text{min}}/\Delta P$  in dimensionless form) and filtration volume. In this mechanism, the pressure drop across the filter increases slowly at the beginning, which will then increase exponentially. The importance of understanding the plugging process is to determine the filter change out time before the pressure drop reaches the region of exponential increase.

To maintain process control the filter should not affect the slurry's composition and the filter should have consistent retention throughout its useful lifetime. Figure 9 shows that filter retention remains fairly constant throughout its lifetime. Table I shows that the filter does not change the percent solids and mean particle size in the slurry, which is extremely important for a CMP process. As long as the solids concentration is not changed before and after filtration, the filter will not alter the bulk particle size distribution. Figure 10 shows the slurry's bulk particle size distribution in the feed and filtrates at 60% and 95% of the CMP5 filter's throughput.

**Implementation Strategy**

Implementation of silica slurry filtration depends on CMP process requirements, space availability, and the characteristics of the slurries. A number of field tests have demonstrated that point-of-use (POU) filtration at the tool can provide the most benefit

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in wafer defect reduction. Table II lists the normalized test results for oxide CMP with POU filtration.

Other filtration locations are at post-dilution, in the distribution loop, and at the slurry supply drum/tote.

It is strongly recommended that the implementation should start at POU filtration with higher retention filters to realize the maximum defect reduction benefits during CMP process development and qualification. To optimize the process, filtration at other locations can be used to supplement POU filter(s) and potentially to extend the life of POU filters.

**Conclusion**

"Large particles" have been detected in CMP slurries using an optical particle counter. SEM evaluation of slurry particles on membrane filters confirmed their existence. These defect-causing large particles may come from agglomeration, local drying of slurry on shipping containers and in the distribution system, and gel formation due to pH shocks during dilution and temperature fluctuations.

Graded-density depth filter can be used effectively to remove the defect-causing large particles without measurable change to slurry composition. Field test data have demonstrated the benefits of filtration on wafer defect reduction during CMP processes.

The optimal strategy to implement filtration in CMP processes can be dependent on site, process, and slurry type. POU filtration with higher retention filters is recommended to realize maximum defect reduction benefits during CMP process development and qualification.

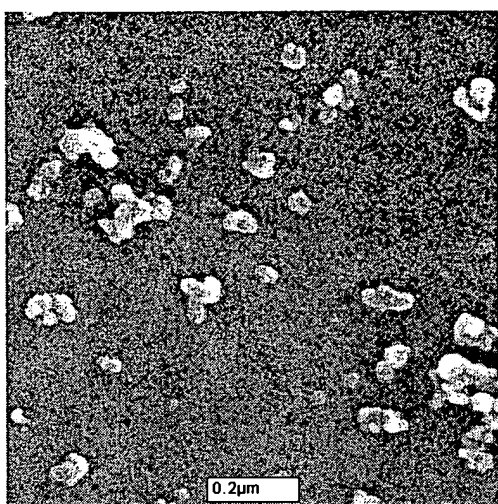
**References**

1. Nagahara, R., et al, The effect of slurry particle size on defect levels for a BPSG CMP process, Proceedings of the CMP Users Group, Vol. 1, No.1, July, 1996
2. CAB-O-SIL Untreated Fumed Silica Properties and Function, Technical brochure, Cabot Corp
3. Yoshida, A., Silica Nucleation, Polymerization, and Growth Preparation of Monodispersed Sols, Chapter 2, The Colloid Chemistry of Silica, Adv. Chem. Ser. 234, 1994
4. Barth, H.G and S.T. Sun, "Particle Size Analysis", Anal. Chem., 57, 151R-175R, 1985

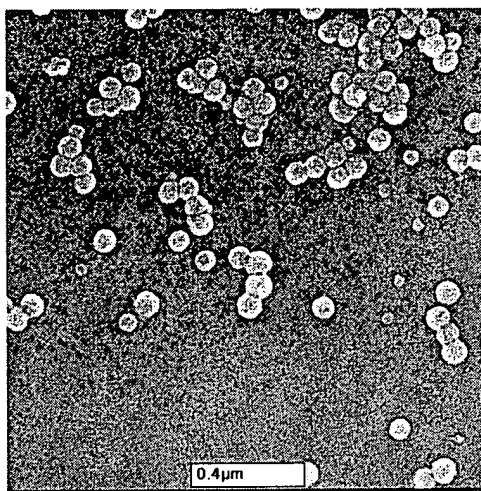
*"POU Filtration of Silica-Based CMP Slurries Using Planargard™ Filters"*

5. J.G. DosRamos and C.A. Silebi, "Size Analysis of simple and complex mixtures of colloids in the submicrometer ranges using capillary hydrodynamic fractionation", Chapter 19, ACS Symposium Series 472, 1990
6. Iler, R. K., The Chemistry of Silica, John Wiley & Sons, New York, NY, 1979

**Figure 1**  
Fumed Silica Aggregates and Colloidal Silica Particles



a. Fumed Silica SEM



b. Colloidal Silica SEM

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Figure 2  
“Large Particles” and Gel in Silica Slurries

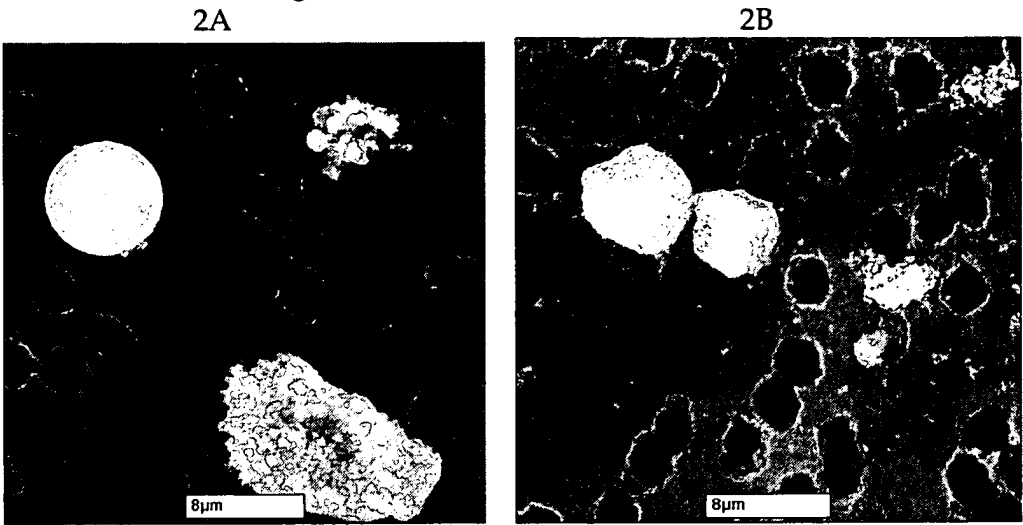
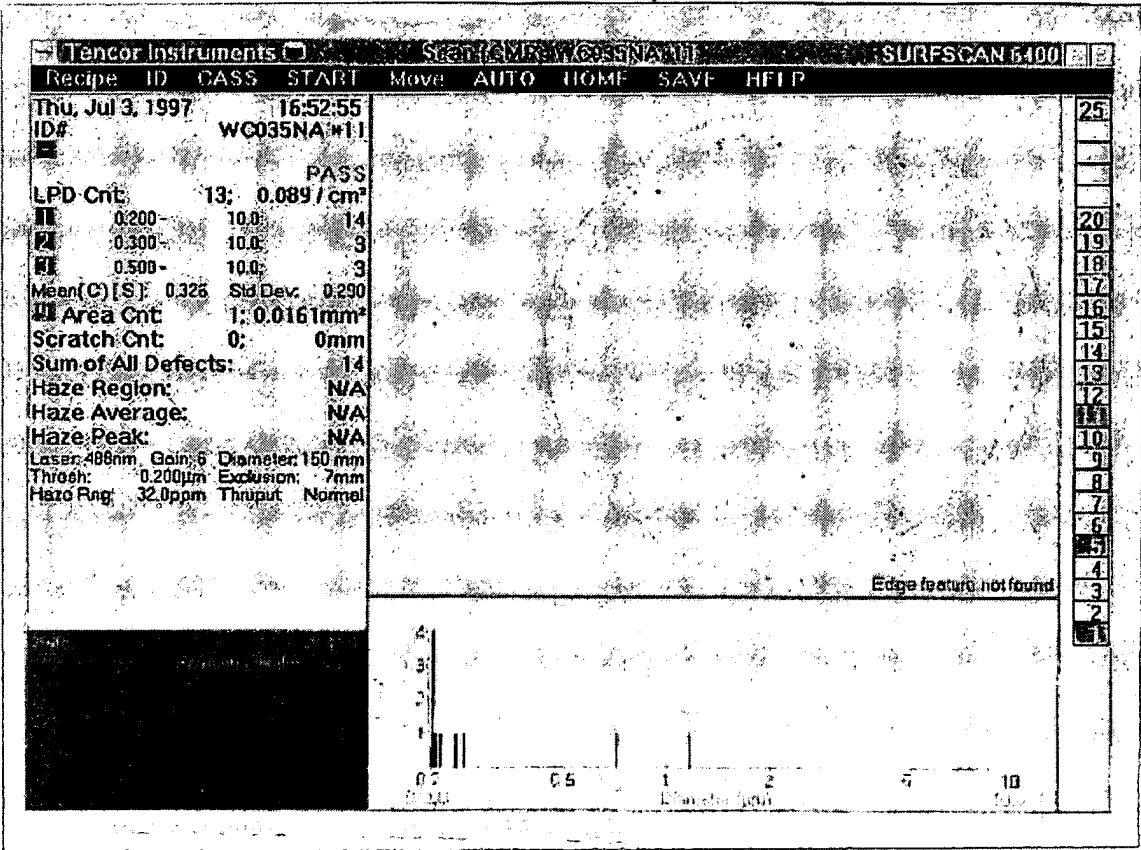


Figure 3 Wafer Scan Result Using Tencor SURFSCAN 6400 for the Wafer Polished with Filtered Slurry



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Figure 4 Wafer Scan Result Using Tencor SURFSCAN 6400 for the Wafer Polished with UN-filtered Slurry

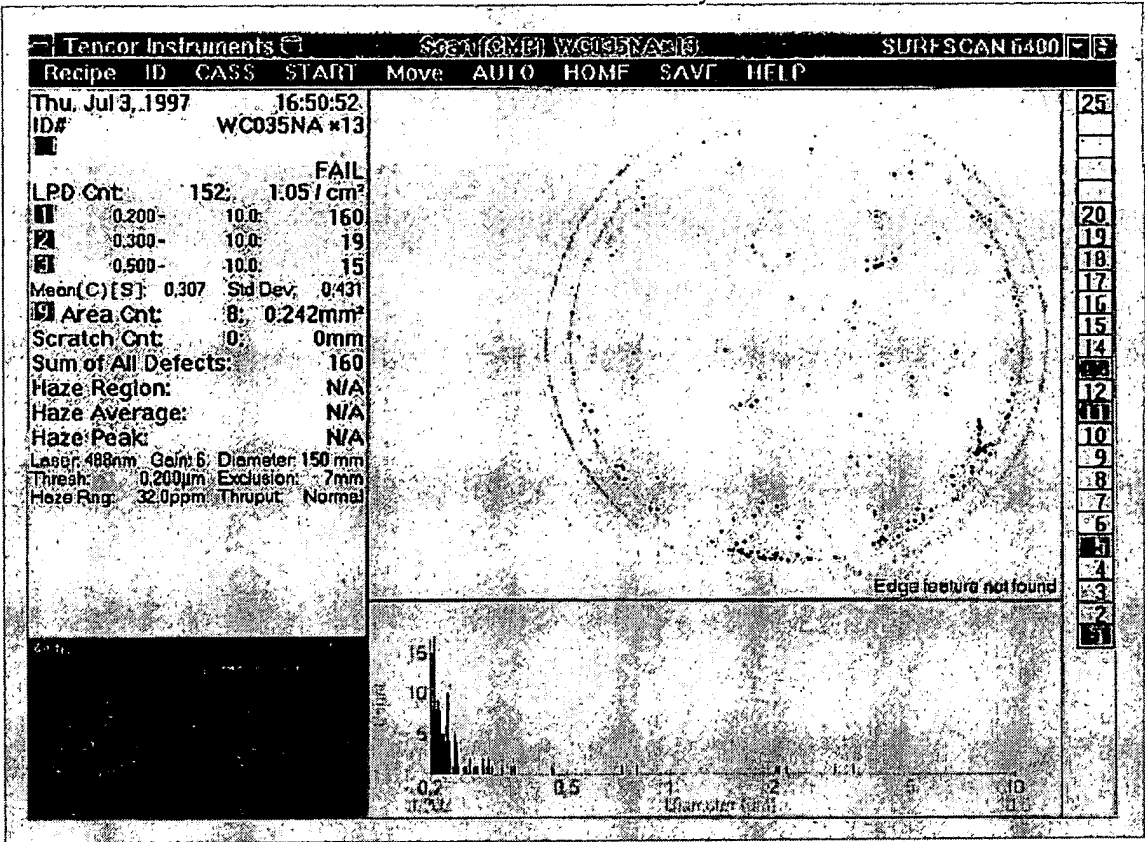


Figure 5

Schematic of Large Particle Counting System

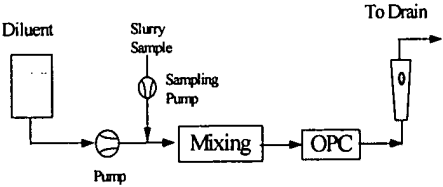
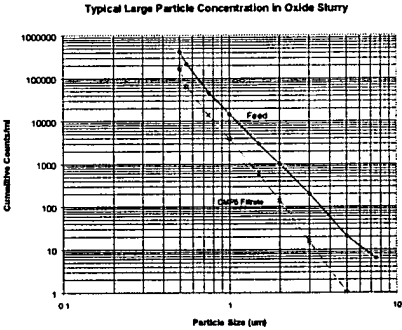


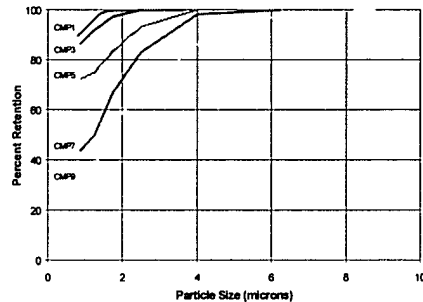
Figure 6



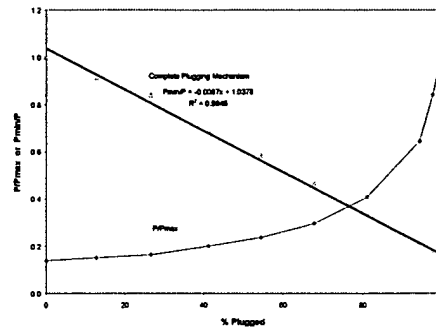


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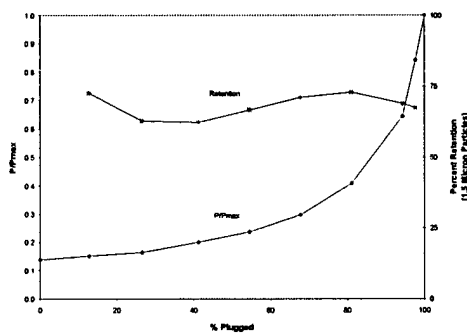
**Figure 7**  
Retention Efficiency of POU  
Planargard™ Filters



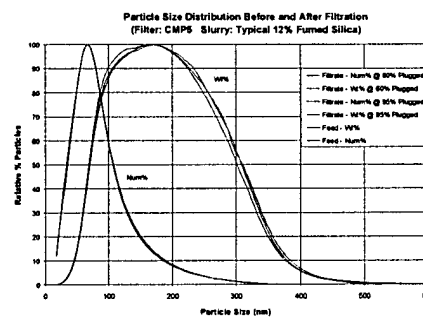
**Figure 8**  
CMP5 Filter Plugging Curve  
in Typical Silica Slurry



**Figure 9**  
Retention Efficiency and Filter Life



**Figure 10**  
Effect of CMP5 Filter on  
Slurry Bulk Particle Size Distribution



**Table I**  
Effect of Filter Plugging on  
Percent Solids and Mean Particle Size in Slurry

	Feed	60% Plugged	95% Plugged
% Solids	12.6	12.4	12.5
DW (nm)	192.3	197.	197.1
DN (nm)	93.3	93.3	94.1

DW: Mean diameter by weight  
DN: Mean diameter by number

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Table II Field Test Results  
Light Point Defect (LDP) Reduction by POU Slurry Filtration

Customer	Slurry	Filters Tested at POU	Normalized LPD Levels
A	Fumed Silica	None	100
		CMP5+CMP3	10
B	Colloidal Silica	None	100
		CMP7+CMP5	30
		CMP3+CMP1	9
C	Colloidal Silica	None	100
		CMP3	33

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